# ESSENTIAL CELL BIOLOGY, FOURTH EDITION
# CHAPTER 3: ENERGY, CATALYSIS, AND BIOSYNTHESIS


## The Use of Energy by Cells

**3-1** Chemical reactions carried out by living systems depend on the ability of some organisms to capture and use atoms from nonliving sources in the environment. The specific subset of these reactions that break down nutrients in food can be described as _____________.
(a) metabolic.
(b) catabolic.
(c) anabolic.
(d)
biosynthetic.

**3-2** When there is an excess of nutrients available in the human body, insulin is released to stimulate the synthesis of glycogen from glucose. This is a specific example of a(n) __________ process, a general process in which larger molecules are made from smaller molecules.
(a) metabolic
(b) catabolic
(c) anabolic
(d) biosynthetic

**3-3** The second law of thermodynamics states that the disorder in any system is always increasing. In simple terms, you can think about dropping NaCl crystals into a glass of water. The solvation and diffusion of ions is favored because there is an increase in _____________.
(a) pH.
(b) entropy.
(c) ions.
(d) stored energy.

**3-4** The energy used by the cell to generate specific biological molecules and highly ordered structures is stored in the form of _____________.
(a) Brownian motion.
(b) heat.
(c) light waves.
(d) chemical bonds.

**3-5** At first glance, it may seem that living systems are able to defy the second law of thermodynamics. However, on closer examination, it becomes clear that although cells create organization from raw materials in the environment, they also contribute to disorder in the environment by releasing _____________.

(a) water.

(b) radiation.

(c) heat.
(d) proteins.

**3-6** If you weigh yourself on a scale one morning, then eat four pounds of food during the day, will you weigh four pounds more the next morning? Why or why not? (Hint: What happens to the atoms from the food you ingested?)

**3-7** In the cytoplasm, materials are organized, separated, and sorted by membranes. Cells exploit the selective permeability of these membranes to partition populations of molecules and generate chemical energy for the cell. Use the principles of the first and second laws of thermodynamics to explain how membranes can be used to produce chemical energy.

**3-8** Indicate whether the following statements are *true* or *false*. If a statement is false, explain why it is false.

A. The second law of thermodynamics states that the total amount of energy in the Universe does not change.
B. The ultimate source of energy for living systems is chlorophyll.
C. $CO_2$ gas is fixed in a series of reactions that are light-dependent.
D. $H_2$ is the most stable and abundant form of hydrogen in the environment.

**3-9** Two college roommates do not agree on the best way to handle the clutter piled up in your dorm room. Roommate 1 explains that chaos is inevitable, so why fight it? Roommate 2 counters that maintaining an organized environment makes life easier in many ways, and that chaos is not inevitable. What law of thermodynamics drives the thinking of Roommate 1? What thermodynamic argument can be used to support Roommate 2?

**3-10** Assume that the average human adult requires 2000 kilocalories per day to sustain all normal processes and maintain a constant weight. If manufactured solar panels could somehow provide power directly to the human body, what size solar panel would be required (in $cm^2$)? Assume there are 10 hours of sunlight per day, and that the usable energy output for a typical solar panel is 850 kJ/$ft^2$ per hour.

*Note*: 1 kcal = 4.184 kJ
$1\ ft^2 = 929.03\ cm^2$

**3-11** In the first stage of photosynthesis, light energy is converted into what other form of energy?
(a) electrical
(b) chemical

(c) potential
(d) kinetic

**3-12** Fill in the blanks, selecting from the choices below.

Light + _________ + _________ → _________ + heat + sugars

$CO$, $CO_2$, $O_2$, $H_2$, $H_2O$, $N_2$, $NO$

**3-13** During respiration, energy is retrieved from the high-energy bonds found in certain organic molecules. Which of the following, in addition to energy, are the ultimate products of respiration?

(a) $CO_2$, $H_2O$
(b) $CH_3$, $H_2O$
(c) $CH_2OH$, $O_2$
(d) $CO_2$, $O_2$

**3-14** Your body extracts energy from the food you ingest by catalyzing reactions that essentially "burn" the food molecules in a stepwise fashion. What is another way to describe this process?

(a) reduction
(b) oxidation
(c) dehydration
(d) solvation

**3-15** Oxidation is a favorable process in an aerobic environment, which is the reason cells are able to derive energy from the oxidation of macromolecules. Once carbon has been oxidized to ________________, its most stable form, it can only cycle back into the organic portion of the carbon cycle through ___________________.

(a) $CO_2$, photosynthesis.
(b) $CH_3$, combustion.
(c) $CO_2$, respiration.
(d) $CO$, reduction.

**3-16** For each of the pairs A–D in Figure Q3-16, pick the more reduced member of the pair.

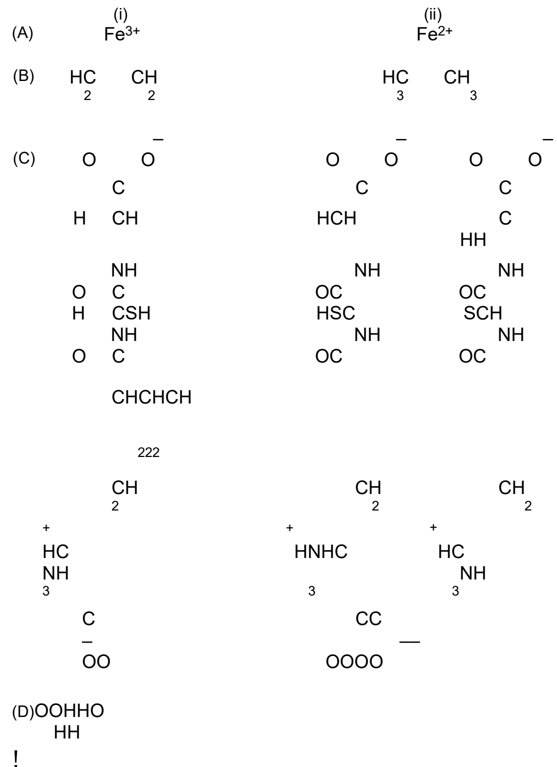


**Figure Q3-16**

**3-17** Oxidation is the process by which oxygen atoms are added to a target molecule. Generally, the atom that is oxidized will experience which of the following with respect to the electrons in its outer shell?
(a) a net gain
(b) a net loss
(c) no change
(d) an equal sharing

**3-18** When elemental sodium is added to water, the sodium atoms ionize spontaneously. Uncharged Na becomes $Na^+$. This means that the Na atoms have been _____________. (a) protonated.
(b) oxidized.
(c) hydrogenated.
(d) reduced.

**3-19** Indicate whether the following statements are *true* or *false*. If a statement is false, explain why it is false.
A. Photosynthetic organisms release only $O_2$ into the atmosphere, while nonphotosynthetic organisms release only $CO_2$.
B. The cycling of carbon through the biosphere first requires the incorporation of inorganic $CO_2$ into organic molecules.
C. The oxidation of one molecule is always coupled to the reduction of a second molecule.
D. During cellular respiration, carbon-containing molecules become successively more oxidized until they reach their most oxidized form, as $CO_2$.

**3-20** Arrange the following molecules in order with respect to their relative levels of oxidation (assign 5 to the most oxidized and 1 to the most reduced).

_______ $CH_2O$ (formaldehyde)

_______ $CH_4$ (methane)

_______ CHOOH (formic acid)

_______ $CH_3OH$ (methanol)

_______ $CO_2$ (carbon dioxide)

**3-21** Oxidation and reduction states are relatively easy to determine for metal ions, because there is a measurable net charge. In the case of carbon compounds, oxidation and reduction depend on the nature of polar covalent bonds. Which of the following is the best way to describe these types of bond?
(a) hydrogen bonds in a nonpolar solution
(b) covalent bonds in an aqueous solution
(c) unequal sharing of electrons across a covalent bond
(d) equal sharing of electrons across a covalent bond

**3-22** Seed oils are often dehydrogenated and added back into processed foods as partly unsaturated fatty acids. In comparison with the original oil, the new fatty acids have additional double carbon–carbon bonds, replacing what were once single bonds. This process could also be described as _____________.
(a) isomerization.
(b) oxidation.
(c) reduction.
(d) protonation.

## Free Energy and Catalysis

**3-23** Chemical reactions that lead to a release of free energy are referred to as "energetically favorable." Another way to describe these reactions is: _____________.
(a) uphill.
(b) uncatalyzed.
(c) spontaneous.
(d) activated.

**3-24** Even though cellular macromolecules contain a large number of carbon and hydrogen atoms, they are not all spontaneously converted into $CO_2$ and $H_2O$. This absence of

spontaneous combustion is due to the fact that biological molecules are relatively __________ and an input of energy is required to reach lower energy states.
(a) large

(b) polar
(c) stable
(d) unstable

**3-25** $\Delta G°$ indicates the change in the standard free energy as a reactant is converted to product. Given what you know about these values, which reaction below is the most favorable? (a) ADP + $P_i$ → ATP $\Delta G°$ = +7.3 kcal/mole (b) glucose 1-phosphate → glucose 6-phosphate $\Delta G°$ = –1.7 kcal/mole (c) glucose + fructose → sucrose $\Delta G°$ = +5.5 kcal/mole (d) glucose → $CO_2$ + $H_2O$ $\Delta G°$ = –686 kcal/mole

**3-26** Catalysts are molecules that lower the activation energy for a given reaction. Cells produce their own catalysts called _____________.
(a)
proteins.
(b) enzymes.
(c) cofactors.
(d) complexes.

**3-27** For each of the following sentences, fill in the blanks with the best word or phrase selected from the list below. Not all words or phrases will be used; each word or phrase should be used only once.
By definition, catalysis allows a reaction to occur more __________________. Chemical reactions occur only when there is a loss of __________________ energy. Enzymes act more __________________ than other catalysts. A catalyst decreases the __________________ energy of a reaction.
activation free selectively
chemical bond kinetic slowly
completely rapidly unfavorable
favorable

**3-28** Figure Q3-28 is an energy diagram for the reaction X→Y. Which equation below provides the correct calculation for the amount of free-energy change when X is converted to Y?
(a) a + b – c
(b) a – b
(c) a – c
(d) c – a

b

a X

free energy

c Y

reaction pathway

!

**Figure Q3-28**

**3-29** Enzymes facilitate reactions in living systems. Figure Q3-29 presents an energy diagram for the reaction X→Y. The solid line in the energy diagram represents changes in energy as the The line shows

reactant is converted to product under standard conditions. dashed

changes observed when the same reaction takes place in the presence of a dedicated enzyme. Which equation below indicates how the presence of an enzyme affects the activation energy of the reaction (catalyzed versus uncatalyzed)?

(a) d – c versus b – c
(b) d – a versus b – a
(c) a + d versus a + b
(d) d – c versus b – a

b
d

a X

free energy

c Y

reaction pathway

!

**Figure Q3-29**

**3-30** The branched diagram in Figure Q3-30 represents several possible reaction pathways that substance X may follow. Each branch point represents two possible reactions, which would give rise to different products. Next to each of these points are values for the uncatalyzed activation energies and **catalyzed activation energies** (in kcal/mole), respectively.

A. Order the final products in the relative amounts you expect them to be produced in the absence of any enzymes (from greatest to least).

B. Order the final products in the relative amounts you expect them to be produced when enzymes for each reaction are present.

C. Compare your answers for parts A and B. How do you think the uncatalyzed reactions could influence the rates of catalyzed reactions inside the cell?

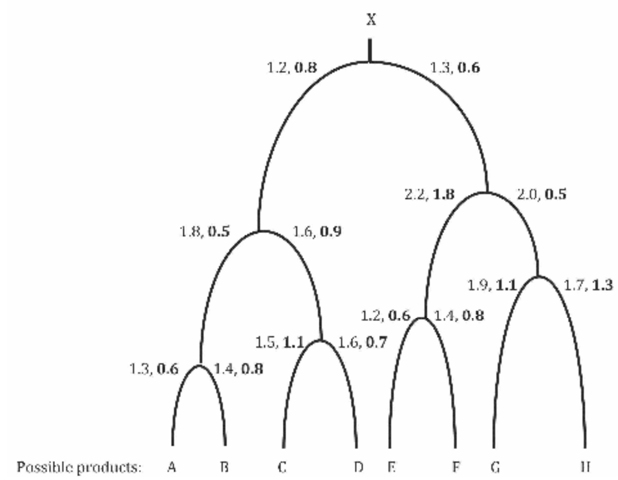


**Figure Q3-30**

**3-31** A chemical reaction is defined as spontaneous if there is a net loss of free energy during the reaction process. However, spontaneous reactions do not always occur rapidly. Favorable biological reactions require _______________ to selectively speed up reactions and meet the demands of the cell.

(a) heat
(b) ATP
(c) ions
(d) enzymes

**3-32** Which of the following statements are *true* or *false*? If a statement is false, explain why it is false.

A. Enzymes lower the free energy released by the reaction that they facilitate.
B. Enzymes lower the activation energy for a specific reaction.
C. Enzymes increase the probability that any given reactant molecule will be converted to product.
D. Enzymes increase the average energy of reactant molecules.

**3-33** $\Delta G$ measures the change of free energy in a system as it converts reactant (Y) into product (X). When [Y] =[X], $\Delta G$ is equal to ______________.

(a) $\Delta G° + RT$
(b) $RT$
(c) ln [X]/[Y]
(d) $\Delta G°$

**3-34** For the reaction Y→X at standard conditions with [Y] = 1 M and [X] = 1 M, $\Delta G$ is initially a large negative number. As the reaction proceeds, [Y] decreases and [X] increases until the system reaches equilibrium. How do the values of $\Delta G$ and $\Delta G°$ change as the reaction equilibrates?

(a) $\Delta G$ becomes less negative and $\Delta G°$ stays the same.
(b) $\Delta G$ becomes positive and $\Delta G°$ becomes positive.
(c) $\Delta G$ stays the same and $\Delta G°$ becomes less negative.

(d) $\Delta G$ reaches zero and $\Delta G°$ becomes more negative.

**3-35** Which of the following is true for a reaction at equilibrium?
(a) $\Delta G = \Delta G°$
(b) $\Delta G° + RT \ln [X]/[Y] = 0$
(c) $RT \ln [X]/[Y] = 0$
(d) $\Delta G + \Delta G° = RT \ln [X]/[Y]$

**3-36** The equilibrium constant ($K$) for the reaction Y→X can be expressed with respect to the concentrations of the reactant and product molecules. Which of the expressions below shows the correct relationship between $K$, [Y], and [X]?
(a) $K = [Y]/[X]$
(b) $K = [Y] * [X]$
(c) $K$
= $[X]/[Y]$
(d) $K = [X] – [Y]$

**3-37** Although the biochemical study of reaction rates and free energies is important for understanding each biological reaction individually, these studies do not provide an accurate picture of what is happening to reactants and products inside the cell. Why not?

**3-38** Isomerization of glucose 1-phosphate to glucose 6-phosphate is energetically favorable. At 37°C, $\Delta G° = –1.42 \log_{10} K$. What is the equilibrium constant for this reaction if $\Delta G° = –1.74$ kcal/mole at 37°C?
(a) 16.98
(b) 0.09
(c) –0.09
(d) 0.39

**3-39** On the basis of the two reactions below, decide which of the following statements are *true* and which are *false*. If a statement is false, explain why it is false.
1: ATP + Y → Y-P + ADP $\Delta G = –100$ kcal/mole
2: Y-P + A → B $\Delta G = 50$ kcal/mole
A. Reaction 1 is favorable because of the large negative $\Delta G$ associated with the hydrolysis of ATP.
B. Reaction 2 is an example of an unfavorable reaction.
C. Reactions 1 and 2 are coupled reactions, and when they take place together, reaction 2 will proceed in the forward direction.
D. Reaction 2 can be used to drive reaction 1 in the reverse direction.

**3-40** The potential energy stored in high-energy bonds is commonly harnessed when the bonds are split by the addition of ________________ in a process called ______________. (a) ATP, phosphorylation.
(b) water, hydrolysis.
(c) hydroxide, hydration.

(d) acetate, acetylation.

**3-41** When the polymer X-X-X… is broken down into monomers, it is "phosphorylyzed" rather than hydrolyzed, in the following repeated reaction:

X-X-X… + P → X-P + X-X… (reaction 1)

Given the Δ*G*° values of the reactions listed in the following table, what is the expected ratio of X-phosphate (X-P) to free phosphate (P) at equilibrium for reaction 1?

6

(a) 1:10

(b) $1:10^4$

(c) 1:1

4

(d) 10:1

X-X-X... + $H_2O$ Æ X + X-X...D*G*° = –4.5 kcal/mole

X + ATP Æ X-P + ADP D*G*° = –2.8 kcal/mole

ATP + $H_2O$ Æ ADP + PD*G*° = –7.3 kcal/mole

!

Figure Q3-41

**3-42** In the case of a simple conversion reaction such as X→Y, which value of Δ*G*° is associated with a larger concentration of X than Y at equilibrium? (Hint: How is Δ*G*° related to *K*?)
(a) Δ*G*° = –5
(b) Δ*G*° = –1
(c) Δ*G*° = 0
(d) Δ*G*° = 1

**3-43** Consider the reaction X→Y in a cell at 37°C. At equilibrium, the concentrations of X and Y are 50 µM and 5 µM, respectively. Use this information and the equations below to answer questions A–E.
$\Delta G° = -0.616 \ln K_{eq}$
$\Delta G = \Delta G° + 0.616 \ln [Y]/[X]$
Recall that the natural log of a number *z* will have a negative value when *z* < 1, positive when *z* > 1, and 0 when *z* = 1.
A. What is the value of $K_{eq}$ for this reaction?
B. Is the standard free-energy change of this reaction positive or negative? Is the reaction X→Y an energetically favorable or unfavorable reaction under standard conditions?
C. What is the value of the standard free energy? Refer to Table 3–1 in the textbook or use a calculator.
D. Imagine circumstances in which the concentration of X is 1000 µM and that of Y is 1 µM. Is conversion of X to Y favorable? Will it happen quickly?

E. Imagine starting conditions in which the reaction X→Y is unfavorable, yet the cell needs to produce more Y. Describe two ways in which this may be accomplished.

**3-44** Hydrolysis reactions are commonly used inside the cell to split high-energy covalent bonds. For each of the three reactions below, use the $\Delta G°$ for each reaction to determine the equilibrium constants ($K$). Assume that each reaction occurs independently of the other two.

$\Delta G°$ (kcal/mole)

Reaction 1: acetyl-P → actetate + P –10.3

Reaction 2: ATP → ADP + P –7.3

Reaction 3: glucose 6-P → glucose + P –3.3

**3-45** If proteins to the dimeric

A and B have complementary surfaces, they may interact form

complex AB. Which of the following is the correct way to calculate the equilibrium constant for the association between A and B?

(a) $k_{on}/k_{off} = K$

(b) $K = [A][B]/[AB]$

(c) $K = [AB]/[A][B]$

(d) (a) and (c)

**3-46** Match the following general equations with the energy diagram that best describes the free-energy transitions along the reaction pathway. Indicate your answer by filling in the equation number in the box under each respective curve. After you have identified a match for each equation, indicate the positions of A, B, and C (if applicable) on the free-energy curves. Not all of the energy diagrams will have a match.

| | | | |
|---|---|---|---|
| 1. | A | B | |
| 2. | A | B | |
| 3. | A | B | C |
| 4. | A | B | C |

!

**Figure Q3-46**

**3-47** The equilibrium constant for complex formation between molecules A and B will depend on their relative concentrations, as well as the rates at which the molecules associate and dissociate. The association rate will be larger than the dissociation rate when complex formation is favorable. The energy that drives this process is referred to as ___________.

(a) dissociation energy.
(b) association energy.
(c) binding energy.
(d) releasing energy.

**3-48** Which of the following statements would not be true of a favorable binding equilibrium?

(a) The free-energy change is negative for the system.
(b) The concentration of the complex remains lower than the concentration of the unbound components.
(c) The complex dissociation rate is slower than the rate for component association.
(d) The binding energy for the association is large and negative.

**3-49** Indicate whether the following statements are *true* or *false*. If a statement is false, explain why it is false.

A. When two macromolecules form a complex, the free energy of the system increases because there is a net increase in the amount of order in the cell.
B. Sequential pathways can help drive unfavorable reactions by siphoning off the products into the next energetically favorable reaction in the series.
C. The cytosol is densely packed with molecules, creating what is more an aqueous gel than a solution.

D. The diffusion rates for smaller molecules in the cytosol are much lower than what is observed for the same molecules in water.

**3-50** The net distance a molecule travels through the cytosol via diffusion is relatively short in comparison with the total distance it may need to travel. This is because movement governed by diffusion alone is a ________________ process that is most effective for the dispersion of small molecules over short distances.
(a) slow
(b) random
(c) regulated
(d) complicated

**3-51** The small molecule cyclic AMP (cAMP) takes about 0.2 second to diffuse 10 µm, on average, the on one end
in a cell. Suppose that cAMP is produced near plasma membrane
of the cell; how long will it take for this cAMP to diffuse through the cytosol and reach the opposite end of a very large cell, on average? Assume that the cell is 200 µm in diameter.
(a) 4 seconds
(b) 16 seconds
(c) 80 seconds
(d) 200 seconds

**3-52** The graph in Figure Q3-52 illustrates the relationship between reaction rates and substrate concentration for an enzyme-catalyzed reaction. What does the $K_m$ value indicate with respect to enzyme–substrate interactions?
(a) the maximum rate of catalysis
(b) the number of enzyme active sites
(c) the enzyme–substrate binding affinity
(d) the equilibrium rate of catalysis

$V_{max}$

rate of reaction

½$V_{max}$

$K_m$ substrate concentration

!

**Figure Q3-52**

**3-53** The graph in Figure Q3-53 illustrates the change in the rate of an enzyme-catalyzed reaction as the concentration of substrate is increased. Which of the values listed below is used to

calculate the enzyme turnover number?
(a) ½$V_{max}$
(b) $K_m$

(c) $V_{max}$
(d) $V_{max} - K_m$

$V_{max}$

rate of reaction

½$V_{max}$

$K_m$ substrate concentration

!

**Figure Q3-53**

**3-54** Protein E can bind to two different proteins, S and I. The binding reactions are described by the following equations and values:

$E + S \rightarrow ES$ $K_{eq}$ for ES = 10
$E + I \rightarrow EI$ $K_{eq}$ for EI = 2

Given the equilibrium constant values, which one of the following statements is *true*? (a) E binds I more tightly than S.
(b) When S is present in excess, no I molecules will bind to E.
(c) The binding energy of the ES interaction is greater than that of the EI interaction. (d) Changing an amino acid on the binding surface of I from a basic amino acid to an acidic one will probably make the free energy of association with E more negative.

**3-55** The study of enzyme kinetics is usually performed with purified components and requires the characterization of several aspects of the reaction, including the rate of association with the substrate, the rate of catalysis, and _____________.
(a) the enzyme's structure.
(b) the optimal pH of the reaction.
(c) the subcellular localization of the enzyme.
(d) the regulation of the enzyme activity.

**3-56** Indicate whether the following statements about enzymes are *true* or *false*. If a statement is false, explain why it is false.
A. Enzymes alter the equilibrium point of a reaction.
B. $V_{max}$ can be determined by measuring the amount of product accumulated late in the reaction.
C. Competitive inhibitors bind irreversibly to the enzyme active site, lowering $V_{max}$.

**3-57** A. You are measuring the effect of temperature on the rate of an enzyme-catalyzed reaction. If you plot reaction rate against temperature, which of the graphs in Figure Q3-57 would you expect your plot to resemble?

B. Explain why temperature has this effect.

1.2.

Reaction rate

0 100 0 100

3. 4.

Reaction rate

0 100 0 100

o
Temperature (C)

!

**Figure Q3-57**

**3-58** Consider a description of an enzymatic reaction pathway that begins with the binding of substrate S to enzyme E, and ends with the release of product P from the enzyme.

$$E + S \rightarrow ES \rightarrow EP \rightarrow E + P$$

In many circumstances,

$$K_m = [E][S]/[ES]$$

A. What proportion of enzyme molecules is bound to substrate when $[S] = K_m$?

B. Recall that when $[S] = K_m$, the reaction rate is $\frac{1}{2}V_{max}$. Does your answer to part A make sense in the light of this rate information?

**3-59** Figure Q3-59 illustrates the amount of energy per molecule for a population in a contained, controlled environment. Most molecules will have the average energy of the population, shown in region 1. The number of molecules in the population with enough energy to be converted to product is shown in region 2. The number of molecules with enough energy to react in the presence of enzyme is shown in region 3. Use this information to explain how enzymes catalyze reactions.

number
of
molecule
s
1

2

3

energy per molecule
molecules with
average energy
!

**Figure Q3-59**

**3-60** Chemical reactions are reversible; they can proceed in both the forward and reverse directions. If the $\Delta G°$ for the reaction Y→X is energetically favorable, how can you explain the fact that not all of the Y molecules will be converted to X molecules?

**3-61** The maximum velocity ($V_{max}$) of an enzymatic reaction is an important piece of information regarding how the enzyme works. What series of measurements can be taken in order to infer the maximum velocity of an enzyme-catalyzed reaction?
(a) the rate of substrate consumption after the system reaches equilibrium, for several reactant concentrations
(b) the rate of product consumption shortly after mixing the enzyme and substrate (c) the rate of substrate consumption at high levels of enzyme concentration (d) the rate of substrate consumption shortly after mixing the enzyme and substrate, for several substrate concentrations

**3-62** What information regarding an enzyme-catalyzed reaction is obtained in a plot of the inverse of the initial velocities against the inverse of the corresponding substrate concentrations?
(a) $1/V_{max}$ and $1/K_m$
(b) $1/V$ and 1/[S]
(c) $V_{max}$ and $K_m$
(d) $V$ and [S]

**3-63** Enzymes A and B catalyze different reactions, but use the same reactant molecule as a substrate. The graph in Figure Q3-63 presents the reaction rates observed when enzyme A and enzyme B are mixed together in a single test tube containing molecule X. What are the $V_{max}$ and the apparent $K_m$ values for each enzyme under these conditions? How might these values change for enzyme B if it were analyzed in the absence of enzyme A? Explain your answer.

(A)

A
XY

B
XZ

(B)

12.5

Enzyme B

10

Initial rate of reaction
7.5

Enzyme A

5

2.5

0 2.5 5 7.5 10 12.5

Concentration of X (mM)

!

**Figure Q3-63**

**3-64** The study of enzymes also includes an examination of how the activity is regulated. Molecules that can act as competitive inhibitors for a specific reaction are often similar in shape and size to the enzyme's substrate. Which variable(s) used to describe enzyme activity will remain the same in the presence and absence of a competitive inhibitor?

(a) $V_{max}$
(b) $V$
(c) $V_{max}$ and $K_m$
(d) $K_m$

## Activated Carriers and Biosynthesis

**3-65** Activated carriers are small molecules that can diffuse rapidly and be used to drive biosynthetic reactions in the cell. Their energy is stored in a readily transferable form such as high-energy electrons or chemical groups. Which of the molecules below is the most widely used activated carrier?

(a) $FADH_2$
(b) NADH
(c) NADPH
(d) ATP

**3-66** Energy cannot be created or destroyed, but it can be converted into other types of energy. Cells use potential kinetic energy to generate stored chemical energy in the form of activated carrier molecules, which are often employed to join two molecules together in

______________ reactions.

(a) oxidation
(b) hydrolysis
(c) condensation
(d) reduction

**3-67** Consider an analogy between reaction-coupling and money. In a simple economy, barter provides a means of direct exchange of material goods. For example, the owner of a cow may have excess milk and need eggs, whereas a chicken owner has excess eggs and needs milk. Provided that these two people are in close proximity and can communicate, they may exchange or barter eggs for milk. But in a more complex economy, money serves as a mediator for the exchanges of goods or services. For instance, the cow owner with excess milk may not need other goods until three months from now, or may want goods from someone who does not need milk. In this case, the “energy” from providing milk to a of “energy”

the economy can be temporarily “stored” as money, which is form used for many transactions in the economy. Using barter and money as analogies, describe two mechanisms that can serve to drive an unfavorable chemical reaction in the cell.

**3-68** You are studying a biochemical pathway that requires ATP as an energy source. To your dismay, the reactions soon stop, partly because the ATP is rapidly used up and partly because an excess of ADP builds up and inhibits the enzymes involved. You are about to give up when the following table from a biochemistry textbook catches your eye.

| hydrolysis reaction | | $\Delta G°$ |
|---|---|---|
| creatine + ATP | enzyme A creatine phosphate + ADP | + 3 kcal/mole |
| ATP + $H_2O$ | enzyme B ADP + phosphate | –7.3 kcal/mole |
| pyrophosphate + $H_2O$ | enzyme C 2 phosphate | –7 kcal/mole |
| glucose 6-phosphate + $H_2O$ | enzyme D glucose + phosphate | –3.3 kcal/mole |

!

**Figure Q3-68**

Which of the following reagents are most likely to revitalize your reaction?
(a) a vast excess of ATP
(b) glucose 6-phosphate and enzyme D
(c) creatine phosphate and enzyme A
(d) pyrophosphate

**3-69** The anhydride formed between a carboxylic acid and a phosphate (Figure Q3-69A) is a high-energy intermediate for some reactions in which ATP is the energy source. Arsenate can also be incorporated into a similar high-energy intermediate in place of the phosphate (Figure Q3-69B). Figure Q3-69C shows the reaction profiles for the hydrolysis of these two high-energy intermediates. What is the effect of substituting arsenate for phosphate in this reaction?

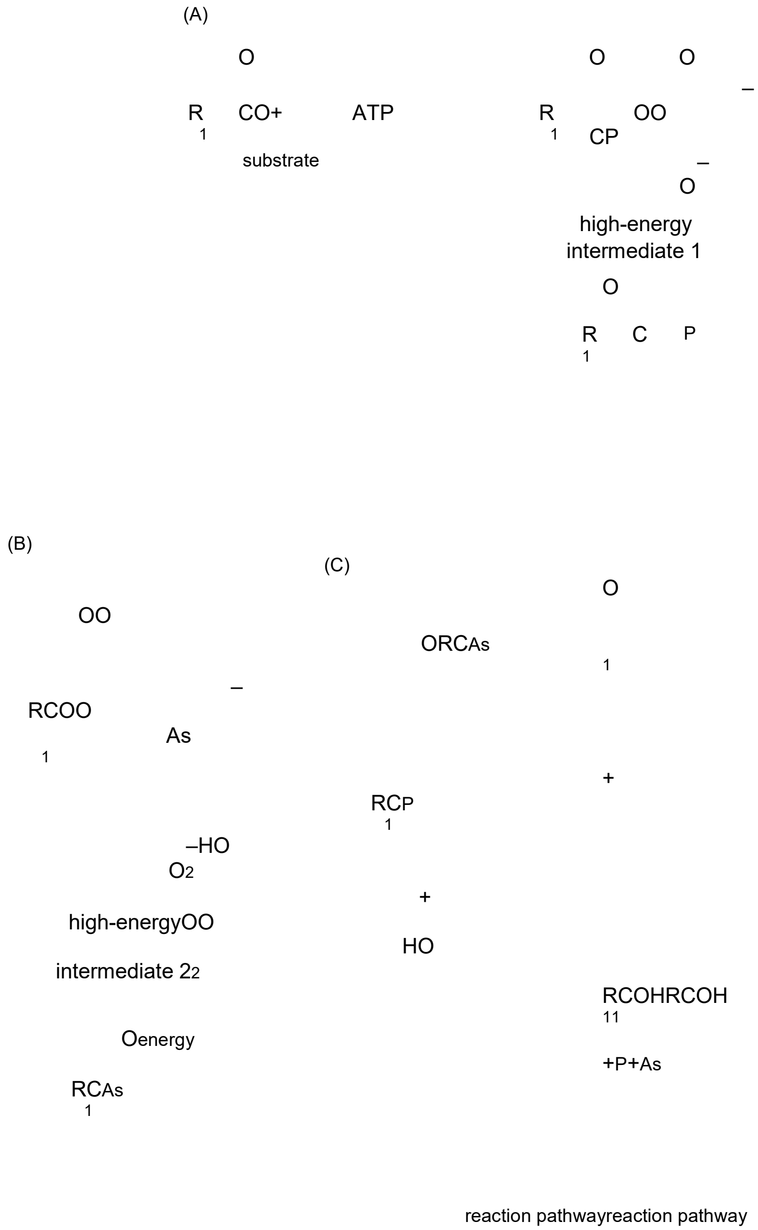


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**Figure Q3-69**

(a) It forms a high-energy intermediate of lower energy.
(b) It forms a high-energy intermediate of the same energy.
(c) It decreases the stability of the high-energy intermediate.
(d) It increases the stability of the high-energy intermediate.

**3-70** In general, there is a positive change in free energy associated with reduction reactions, and of them are coupled with oxidation reactions. The last step in the biosynthesis of cholesterol involves the reduction of a carbon–carbon double bond. What activated carrier molecule is used in this reaction (and generally for the reduction of lipids) and how would this reaction be influenced by the levels of available ATP?

**3-71** The synthesis of glutamine from glutamic acid requires the production of an activated intermediate followed by a condensation step that completes the process. Both amino acids are shown in Figure Q3-71.

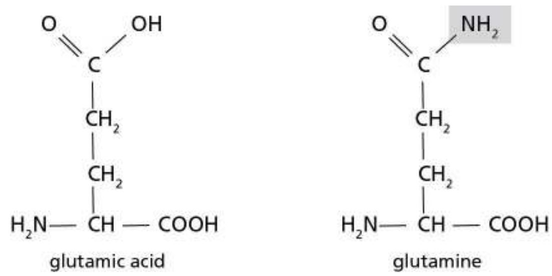


**Figure Q3-71**

Which molecule is added to glutamic acid in the activation step?
(a) phosphate
(b) $NH_3$
(c)
ATP
(d) ADP

**3-72** The synthesis of glutamine from glutamic acid requires the production of an activated intermediate followed by a condensation step that completes the process. Both amino acids are shown in Figure Q3-72.

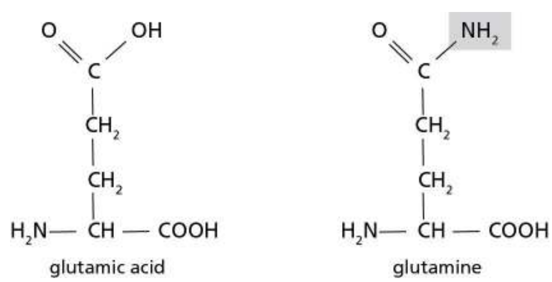


**Figure Q3-72**

In the condensation step, _______________ is displaced by ________________. (a) OH, $NH_3$.
(b) ADP, $NH_2$.
(c) ATP, $NH_3$.
(d) phosphate, $NH_3$.

**3-73** NADH and NADPH are activated carrier molecules that function in completely different metabolic reactions. Both carry two additional ________ and one additional _____________. This combination can also be referred to as a hydride ion.
(a) protons, electron.
(b) electrons, phosphate.
(c) hydrogens, electron.
(d) electrons, proton.

**3-74** Coenzyme A can be converted to acetyl CoA, which is an important activated carrier molecule that has a central role in metabolism and can be used to add two carbons in each successive cycle of fatty acid synthesis.

A. Identify the location and type of high-energy bond in the acetyl CoA molecule shown in Figure Q3-74.
B. How does the bond energy help promote the synthesis of fatty acids?
C. What function does the rest of the coenzyme A molecule serve in these reaction pathways?

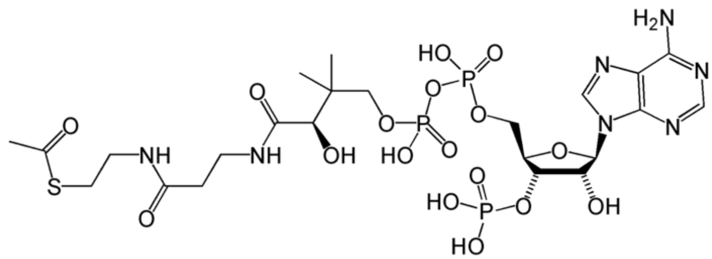


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**Figure Q3-74**

**3-75** The addition of a new deoxynucleotide to a growing DNA chain requires more energy than can be obtained by the hydrolysis of ATP to ADP + Pi. What alternative series of reactions is used, and how does this help overcome the energy barrier for DNA synthesis?

# ANSWERS

**3-1** (b)

**3-2** (c)

**3-3** (b)

**3-4** (d)

**3-5** (c)

**3-6** No, you will not weigh four pounds more the next morning because only a small portion of the mass of the food will form components of the body. Much of the mass of food is either released as $CO_2$ and $H_2O$ that are breathed out into the atmosphere or converted into materials excreted as waste products.

**3-7** When one type of molecule accumulates at a higher concentration on one side of the membrane, the molecules become "organized" by having their movement limited to the space they occupy. The second law of thermodynamics indicates that, if allowed to do so, the molecules would move across the membrane until there is an equal distribution of molecules on either side. The accumulation of molecules on one side of the membrane represents a store of potential energy. The first law of thermodynamics tells us that this energy will not be lost, but rather converted into a different type of energy. First, when the molecules are then allowed to move across the membrane, this potential energy is converted into kinetic energy. The kinetic energy of molecules moving through a protein channel to cross the membrane is often linked to conformational changes in the protein, promoting specific chemical reactions.

**3-8** A. False. The second law of thermodynamics states that components of any system move toward greater disorder. It is the first law of thermodynamics that states that energy is neither created nor destroyed.

B. False. The ultimate source of energy for living organisms is sunlight.

C. False. The fixation of carbon from $CO_2$ occurs independently of light.

D. False. The most stable form of hydrogen is $H_2O$.

**3-9** The second law of thermodynamics supports Roommate 1's view. It is favorable for a system to become less ordered. However, if the energy used to create an ordered environment in the room is accompanied by enough release of heat, the Universe will become more disordered as the room becomes more organized. Thus, while increasing chaos is inevitable, the room—like a cell—can be kept highly organized, by interconverting types of energy.

**3-10** Conversion factors:

1 kcal = 4.184 kJ

1 $ft^2$ = 929.03 $cm^2$

If there are 10 hours of sunlight each day hitting the solar panel, there are 8500 kJ/ft$^2$

produced per day. The average adult human requires 8368 kJ per day; thus, with a conventional solar panel, we would require a surface area of about a square foot, or more precisely in cm$^2$:

$8368 \text{ kJ}/X = 8500 \text{ kJ}/929.03 \text{ cm}^2$

929.03 µltiply 8368/8500 = $X$

$X = 914.57 \text{ cm}^2$

**3-11** (a) **or** (d)

**3-12** Light + $\mathbf{H_2O}$ + $\mathbf{CO_2}$ → $\mathbf{O_2}$ + heat + sugars

**3-13** (a)

**3-14** (b)

**3-15** (a)

**3-16** A—ii; B—ii; C—i; D—ii. "More reduced" means having more electrons; gain of electrons can result in an increased negative charge or a decreased positive charge and can be due to an increase in the number of hydrogen atoms in a molecule.

**3-17** (b)

**3-18** (b)

**3-19** A. False. Plants, as well as photosynthetic algae and bacteria, perform both photosynthesis and respiration. This means that photosynthetic organisms release both $O_2$ and $CO_2$ into the atmosphere.

B. True.

C. True. This forms the basis for redox pairs.

D. True.

**3-20** __3__ $CH_2O$ (formaldehyde)

__1__ $CH_4$ (methane)

__4__ CHOOH (formic acid)

__2__ $CH_3OH$ (methanol)

__5__ $CO_2$ (carbon dioxide)

**3-21** (c)

**3-22** (b)

**3-23** (c)

**3-24** (c)

**3-25** (d)

**3-26** (b)

**3-27** By definition, . reactions
catalysis allows a reaction to occur more **rapidly**Chemical
occur only when there is a loss of **free** energy. Enzymes act more **selectively** than other catalysts. A catalyst decreases the **activation** energy of a reaction.

**3-28** (d)

**3-29** (b)

**3-30** The lower the activation energy, the larger the number of molecules that have the energy required to overcome the energy barrier. When no enzymes are present, the uncatalyzed activation energies will determine the relative rates at which the substrate undergoes either reaction.

A. Following this principle, the relative amounts of products in the absence of the necessary enzymes (from greatest to least) are: C, D, A, B, H, G, E, F.

B. In the presence of the enzymes required to catalyze the two different reactions represented by each branch, we should expect to see a different distribution of products: G, H, E, F, A, B, D, C.

C. Although we can make these predictions based on activation energies, there are many other factors that determine how fast a certain product will accumulate: reactant concentration, catalytic efficiency of the enzyme in question, and the relative reactivity of the product, to name a few. If a reaction has a very low uncatalyzed activation energy, it could occur spontaneously at a rapid rate, which would decrease the concentration of substrate available for the enzyme-catalyzed reaction. If this is the case, the relative abundances predicted in part B will change.

**3-31** (d)

**3-32** A. False. Enzymes do not affect the initial energy of the reactants nor the final energy of the products after the reaction is complete, which are the values that determine the change in free energy of a reaction.

B. True.

C. True.

D. False. By lowering the energy of activation, enzymes increase the number of molecules in a population that can overcome the activation barrier.

**3-33** (d)

**3-34** (a)

**3-35** (b)

**3-36** (c)

**3-37** Chemical reactions inside the cell do not reach a state of equilibrium because both reactants and products are typically used in more than one set of reactions, which means their a reverse
concentrations are constantly fluctuating. As result, the forward and
reaction rates are almost never identical.

**3-38** (a)

**3-39** A. True.
B. True.
C. True.
D. False. This is false for two reasons: (1) reaction 2 is unfavorable, as indicated by the positive free-energy change associated with the reaction; (2) the reverse reaction, although possibly more favorable, will yield the product for reaction 1, not reactants to help drive it forward.

**3-40** (b)

**3-41** (c) Reaction 1 can be written as the sum of the three reactions given, because the ATP used in step 2 is restored in step 3.

X-X-X… + $H_2O$ → X + X-X… $\Delta G°$ = –4.5 kcal/mole
X + ATP → X-P + ADP   $\Delta G°$ = –2.8 kcal/mole
ADP + P → ATP + $H_2O$   $\Delta G°$ = +7.3 kcal/mole

Because $\Delta G°$ values are additive, $\Delta G°_{total} = 0$, and if $\Delta G° = 0$, $K_{eq} = 1$, meaning that [products]/[reactants] = 1, and the ratio of X-P to P is 1:1.

**3-42** (d)

**3-43** A. $K_{eq}$ = [Y]/[X] = 5 µM/50 µM = 0.1
B. The standard free-energy change, $\Delta G°$, is positive because $K_{eq}$ is less than 1.

Under standard conditions (equal concentrations of X and Y), the reaction X→Y is unfavorable.

C. $\Delta G° = -0.616 \ln K_{eq} = -0.616 \ln 0.1 = (-0.616)(-2.3) = 1.4$ kcal/mole.

D. Yes, the conversion is favorable because the value of [Y]/[X] is less than the equilibrium value. However, the speed of the reaction cannot be determined from the free-energy difference. For example, combustion of this piece of paper is a highly favorable reaction, yet it will not happen in our lifetime without a catalyst.

E. The cell may directly couple the unfavorable reaction to a second, energetically favorable reaction whose negative $\Delta G$ has a value larger than the positive $\Delta G$ of the X→Y reaction; the coupled reaction will have a $\Delta G$ equal to the sum of the component reactions. Alternatively, more X will be converted to Y if the concentration of Y drops; this may happen if Y is converted to Z in a second reaction or if Y is exported from the cell or compartment where the X→Y reaction occurs.

**3-44** $K$ can be easily calculated from the standard free-energy values by solving the standard free-energy equation ($\Delta G° = -1.42 \log K$) for $K$ ($K = 10^{\Delta G°/-1.42}$).

Reaction 1: $K = 10^{7.25}$

Reaction 2: $K = 10^{5.14}$

Reaction 3: $K = 10^{2.32}$

**3-45** (d)

**3-46**

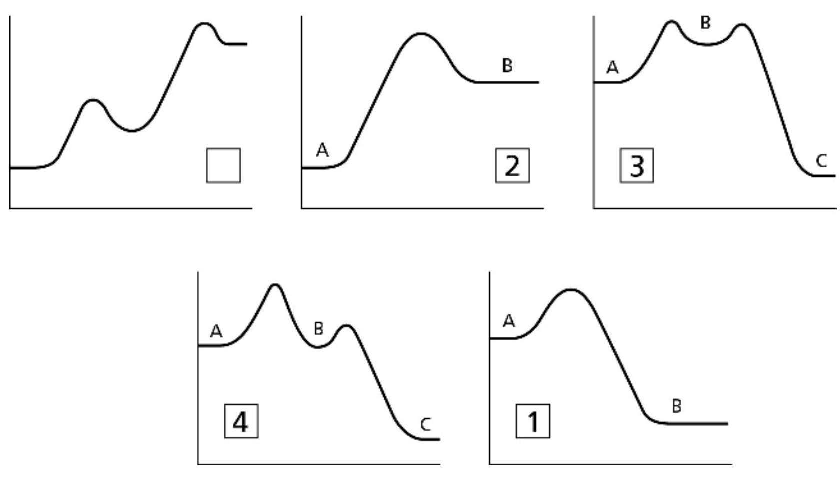


**Figure A3-46**

**3-47** (c)

**3-48** (b)

**3-49** A. False. Even nonspecific interactions between macromolecules can be favorable if there is a large number of water molecules and ions displaced at the interaction interface. This would lead to an overall increase in disorder, even though the two larger molecules become associated and more ordered.

B. True.

C. True.

D. False. Small molecules diffuse through the cytosol nearly as rapidly as they diffuse in water.

**3-50** (a)

**3-51** (c)

**3-52** (c)

**3-53** (c)

**3-54** Choice (c) is true. The binding energy is the standard free energy of the binding reaction, and thus is proportional to ln $K_{eq}$. As the binding energy increases, the equilibrium constant are false,
for the association reaction becomes larger. Choices (a) and (b)
because although E binds S more tightly than it does I, some E molecules will still be bound to I molecules. Choice (d) is false; although not enough information is given to be certain, it is more likely that binding would be weakened by this change, making the free energy of association more positive.

**3-55** (d)

**3-56** A. False. An enzyme catalyzes its reaction in both directions, lowering the energy of activation for both the forward and reverse reactions. Enzymes do not affect the free energy of the reactants and products are the same, and thus they do not affect the reaction equilibrium.

B False. Initial reaction velocities are measured to determine $V_{max}$.

C. False. Competitive inhibitors bind reversibly to an enzyme's active site.

**3-57** A. Graph 1 is correct.

B. By increasing thermal motion, increasing the temperature increases the number of collisions of sufficient energy to overcome the activation energy. An increase in temperature will thus increase the reaction rate initially. However, enzymes are proteins and are held together by noncovalent interactions, so at very high temperatures the enzyme will begin to denature and the reaction rate will fall.

**3-58** A. When [S] is substituted for $K_m$ in the equation, it becomes clear that [E] = [ES]. Thus, half of the enzyme molecules are free and half are bound to the substrate. B. Yes. If half of the enzyme molecules are bound to the substrate, it makes intuitive sense that the reaction rate is half of the maximum possible rate, or half of the rate observed when all of the enzyme molecules are bound to the substrate.

**3-59** The presence of enzyme in the mixture of reactant molecules does not change the energy distribution of the population of molecules. Their average energy will remain the same, and there still will be only a very small proportion of the molecules with high energy. Enzyme catalysis increases the total number of molecules that have sufficient energy to participate in the reaction because the total energy required per molecule that reacts is lowered.

**3-60** Even when the forward reaction is highly favorable, it is important to keep in mind that molecules exist as part of a population, and each member of a given population has a varying level of energy per molecule. Statistically speaking, there will always be some molecules that have sufficient energy to reach the energy of activation for the back reaction X→Y, even though the proportion of molecules with this energy will be much lower than that for the forward reaction Y→X. As more and more X molecules are converted to Y molecules, eventually the Y molecules in the mixture outnumber the X molecules to such a large extent that the fluxes in the backward and forward directions become equal; it is here that the reaction reaches its equilibrium point.

**3-61** (d)

**3-62** (a)

**3-63** Under the mixed conditions, enzyme A has a $V_{max}$ of 6 and an apparent $K_m$ of 1 μM X; enzyme B has a $V_{max}$ of 10 and an apparent $K_m$ of 3 μM. Because enzyme A has a higher affinity for substrate, it more quickly binds to reactant X and converts it into the product Y, lowering the effective concentration of X reactant available for enzyme B. If enzyme B were tested separately, the $V_{max}$ should stay the same, but the $K_m$ might be smaller and be a more accurate reflection of the binding affinity of enzyme B for the reactant molecule X.

**3-64** (a)

**3-65** (d)

**3-66** (c)

**3-67** Barter is analogous to the direct coupling of a favorable to an unfavorable reaction by a single enzyme. Money is analogous to the storage of energy from a favorable reaction in the form of high-energy bonds in an activated carrier molecule. Such activated carrier molecules can later be used to drive a huge variety of other unfavorable reactions in the cell, either by being hydrolyzed to provide the needed energy for a reaction or by transferring an activated chemical group to another molecule.

**3-68** (c) An excess of ATP will initially restore the reactions, but as ATP is hydrolyzed, ADP will build up and inhibit the enzymes again. Pyrophosphate does not look like ATP and is therefore unlikely to be used by the enzymes as an alternative energy source. Pyrophosphate + enzyme D will just heat things up. What you need is a high-energy source of phosphate that can convert ADP back to ATP. Because the $\Delta G°$ of the reaction
ATP + creatine → ADP + creatine phosphate

catalyzed by enzyme A is greater than zero, the addition of creatine phosphate and enzyme A can be used to form ATP from ADP, regenerating the ATP while also forming creatine as a waste product.

**3-69** Choice (c) is correct. The activation energy of the arsenate compound is extremely low, as can be seen from the reaction profile, meaning that its high-energy intermediate is very unstable and will be spontaneously hydrolyzed more rapidly than the phosphate compound. In fact, this hydrolysis occurs rapidly without enzyme catalysis, even in cellular conditions. Arsenate is therefore quite deleterious for living organisms.

**3-70** NADPH is the activated carrier used in the final reduction reaction to produce cholesterol. The rate of this reaction will depend upon the concentration of NADPH, the regeneration of which depends upon ATP hydrolysis. If ATP levels are low, then we can expect cholesterol

that the levels of NADPH will be correspondingly low. The rate of synthesis will be lower than if the cell is in a high-energy state with abundant levels of ATP, and consequently high levels of NADPH.

**3-71** (a)

**3-72** (d)

**3-73** (d)

**3-74** A. The thioester bond is the high-energy bond, boxed in Figure A3-74.

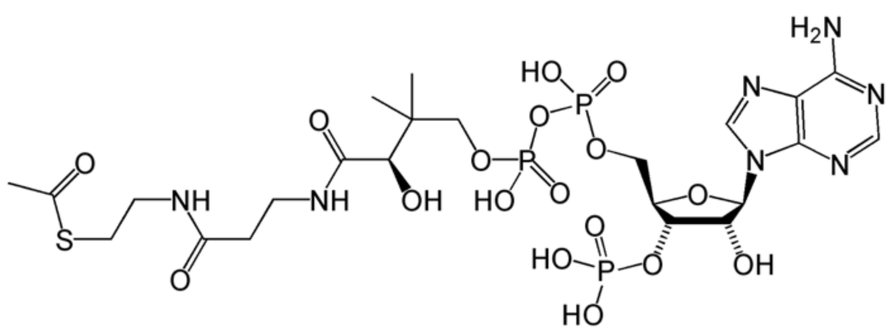


**Figure A3-74**

B. The generation of long-chain fatty acids requires the generation of new carbon–carbon bonds and the reduction of carbon–oxygen bonds. The energy stored in the acetyl CoA thioester bond promotes the addition of new carbons to an elongating fatty acid chain, two carbons at a time. However, the high-energy electrons required to reduce the carbonyl bond are derived from a second type of molecule, NADPH.

C. The rest of the acetyl CoA molecule provides a specific surface recognized by the enzymes that catalyze reactions in which acetyl CoA is required.

**3-75** The hydrolysis of ATP to ADP is favorable, with a Δ*G* between –11 and –13 kcal/mole. However, this is not sufficient to drive the addition of a nucleotide to the end of a growing DNA strand. Instead, two reactions are used. The first reaction converts ATP to a DNA-linked AMP residue when a phosphodiester bond is formed during DNA synthesis; simultaneously, a pyrophosphate molecule ($PP_i$) is released. In the second reaction, the $PP_i$ is hydrolyzed to form two molecules of $P_i$. This second reaction is also favorable, providing roughly another –13 kcal/mole. Adding up the $\Delta G$ for the entire process, there will be about –26 kcal/mole to drive the addition of the nucleotide to the growing DNA chain, which is sufficient to drive the reaction strongly in one direction.